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Dynamics of the Collinear Be + FH → BeF + H Reaction

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Results of a study of the collinear reaction Be + FH(v_1) → BeF(v_2) + H are summarized. The surface was obtained by an ab initio first-order wave function CI calculation. Dynamics were studied using quasi-classical trajectories. A comparison study was made using a LEPS surface with similar characteristics. The ab initio surface was found to give rise to quite special results. Because of interest in the analogous Ba + HF system, the effect of varying the mass of the atom was observed.

Introduction

Recently we reported an ab initio calculation of the potential surface for the collinear reaction Be + FH(v_1) → BeF(v_2) + H and a quasi-classical trajectory study of the dynamics on the surface.[1] Our interest in this system arose from the results of an experimental study of the reaction Ba + HF → BaF + H.[2] Contrary to expectations based on model systems of comparable exoergicity and mass combination,[3] it was found that a small fraction of the system energy appeared as product vibration. It was postulated that some special feature of the potential energy surface was responsible for this behavior. More recent experimental studies with other alkaline earth atoms[4] have added to the store of available information.

The great majority of theoretical studies of the dynamics of A + BC triatomic exchange reactions have employed the LEPS or closely related potential energy surfaces.[5] Simple to use, with some, but not too many adjustable parameters, these surfaces have proven to be remarkably good for some systems. However, their quantum mechanical ancestry is in the simplest valence bond theory, and one would anticipate that their utility would be limited where multiple valence structures are required. In particular, the alkaline earth plus hydrogen halide systems which proceed from essentially covalent bonding in the reactant channel to quite ionic in the product channel constitute such a case.

Results and Discussion

In an ab initio study of the electronic structure of a system the difficulty and cost are closely related to the number of electrons. Thus we chose to investigate the reaction Be + FH → BeF + H. While members of the same group in the periodic table, beryllium and barium are probably more unlike than like; nevertheless we believe that in a very general sense the systems are related, and that the surfaces, while differing in detail, should share some common features. The ground (electronic) state of the reactants Be (^{1}S) + HF($^1\Sigma$) is described by a closed shell electronic configuration, while the products, BeF($^2\Sigma$) + H(^{2}S), require an open shell configuration. Therefore, a configuration interaction (CI) approach is required to obtain the ground state $^1\Sigma$ surface. A first order CI wave function using a moderate sized basis set of Slater atomic orbitals was used. The configurations were carefully selected to treat the asymptotic channels at an equivalent level of approximation. Details of the calculation can be found in ref 1. For comparison, a LEPS surface was constructed with parameters selected to reproduce the barrier height and position of the ab initio surface. Contour plots of the two surfaces are shown in Figure 1.

Simple inspection of the contour plots reveals the important differences which are reflected in the dynamics. On the ab initio surface vibration is poorly coupled to translation as the reactants approach; the energy rises, but there is little distortion of the equilibrium position of the molecule. The pass to the product valley appears at the side of the reactant valley. The reaction path (not shown) would have to turn quite abruptly to pass over the col. This is contrasted with the LEPS surface where translation and vibration couple smoothly and the reaction path curves gradually over the barrier. The difference is easily understood; the ab initio surface reflects the rather sharp change in configuration as the nature of the bonding in the system changes, while the LEPS surface is smoothly covalent.

The collision dynamics was investigated using the quasi-classical trajectory method. The reaction was studied over a range of translational energies for both HF(v_1=0) and HF(v_1=1). The most striking feature of the

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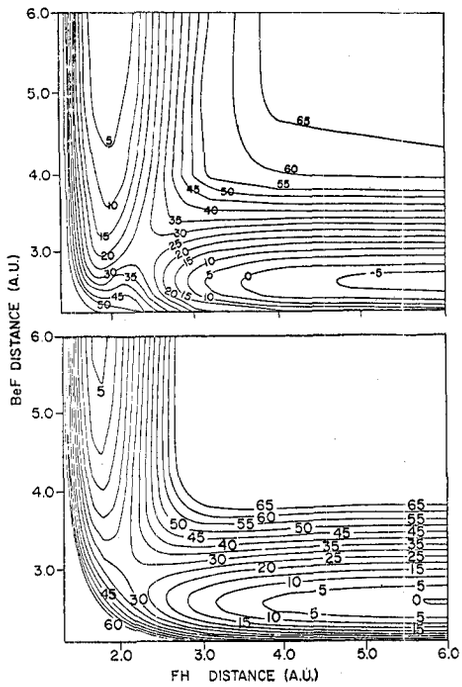

Figure 1. Potential surfaces for the collinear reaction Be + FH – BeF + H. Reactants enter from the upper left, products exit from the lower right. Equipotential contours are indicated in kilocalories per mole relative to separated reactants. Distances are expressed in bohr radii (AU). The upper panel shows the ab initio result, the lower the LEPS surface.

results was the contrast in behavior between the vibrationally cold and vibrationally excited systems. With cold reactants, the reaction probability rose rather gradually from the threshold energy, and remained less than unity over the full range of energies. With excited reactants, the probability rose sharply from threshold, and remained at unity over a wide range of translational energies. The disposal of energy in the products showed a similar contrast; with Be + FH(v_1=0) there was some vibrational excitation of the products near the threshold energy, but, as the translational energy increased, products were formed with decreasing vibrational excitation. At energies a few kilocalories per mole above threshold an average of less than 10% of the total energy appears as product vibration. With Be + FH(v_1=1), a significantly larger portion of the system energy appeared as product vibration, and the vibrational distributions were broader and peaked toward higher excitations.

Figure 2 illustrates this result. Included are results from the LEPS surface as well. With vibrationally cold reactants the contrast is pronounced. The very low vibrational excitation of the products is indeed a special feature of the ab initio surface.

These results are promising. The ab initio calculation does yield a surface which is quite different from a LEPS surface. The collinear dynamics does show a preference for low vibrational excitation of the products. Further, vibrational excitation of the molecule changes the results significantly. However, caution must be exercised in making comparison with experiment. Perhaps most importantly, this is a collinear calculation. Preliminary results at the SCF level indicate a rise in the energy as the collinear geometry is broken, but this is by no means definite. Even if this is so, it is not easy to predict what the effect of the full dimensionality will be on the system. Progress has been made in relating one- to three-dimensional calculations,[6] but, again, the focus has been on systems described by a LEPS-type surface. Another serious difficulty is that the theoretical system is Be + FH,

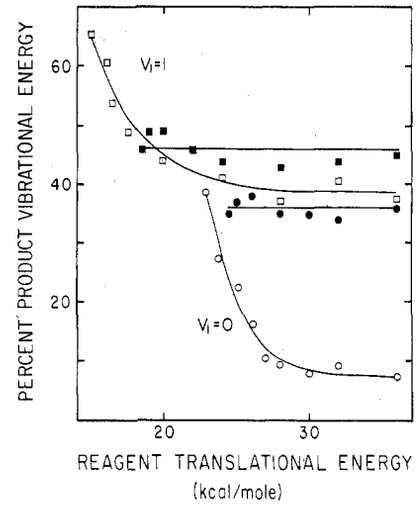

Figure 2. Energy disposal in the products for Be + FH(v_1) → BeF + H. Circles represent ground vibrational state reactants, squares the first excited state. Open symbols are results on the ab initio surface, filled symbols on the LEPS. Curves have been drawn to guide the eye.

TABLE I: The Effect of Altering the Mass of the Atom in the Be + FH Reaction

E_{trans}, kcal/mol	9.0 amu mass		137.3 amu mass	
	P_R[a]	% E_{vib}	P_R	% E_{vib}
		v_1 = 0		
22.9	0.21	38	0.06	39
28.0	0.96	9.5	0.96	17
		v_1 = 1		
15.0	0.25	65	1.0	67
28.0	1.0	38	1.0	58

[a] P_R is the reaction probability.

while the experiments have included Ba, Ca, or Sr + HF. The sharp feature in the potential surface as the configuration changes might be expected in all of these systems, but its precise location will certainly differ, perhaps in dynamically significant ways.

The transition from Be to Ba is also reflected in a change in mass. We explored the effect of this change alone by following trajectories on the ab initio surface for Be + FH, but with masses appropriate to Ba + FH. Results are shown in Table I, with the corresponding Be + FH results for comparison. It is evident that the mass change causes quantitative, but not qualitative, differences. The reaction is still sensitive to the vibrational excitation of the reactants, the cold reactants resulting in product vibration significantly less than that from the vibrationally excited reactants. However it is seen that the mass change does increase the fractional vibrational excitation at higher energies for both cases.

Conclusion

Much of our understanding of the interrelationship between the potential surface and dynamics has come from quasi-classical trajectory studies on simple model surfaces, particularly LEPS. There has resulted a somewhat detailed picture of the connection between the barrier height and position and the energy requirements and energy disposal in the reaction. Studies of systems of more than three atoms, an area pioneered by Don Bunker, have shown that this picture is difficult to extrapolate.[7] Our results presented here extend this caveat; even in triatomic systems special features of the potential surface can give rise to unexpected dynamics. Moreover, we suggest that these exceptions, as is so often the case, may be very numerous.

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Thermal Dissociation Rate of Ethane at the High Pressure Limit from 250 to 2500 K

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Experimental measurements of the thermal decomposition rate of ethane from 1330 to 2500 K, extrapolated to high pressure limit rate constants using RRK theory, are found to be in accord with previous work. Combining low temperature methyl radical recombination rate constants with ethane decomposition rate constants results in a coherent set of rate measurements for this process at the high pressure limit from 250 to 2500 K. RRKM calculations using several models for the critical configuration were performed and compared with this data base. A critical configuration model using a minimum density-of-states criterion for defining the critical configuration and a hindered rotor description for the four degrees of freedom that are converted from vibrations in the molecule to free rotations of the methyls was found to give a substantially better description of the data than any vibrator or free rotor model. Since it was not possible to fit the experimental temperature dependence of the high pressure limit recombination rate constant with any critical configuration model, one must conclude either that the minimum-density-of-states version of the RRKM model is incorrect, or that the strong-collision assumption inherent in extrapolating the high temperature decomposition rate data leads to a substantial underestimate of the high pressure limit rate constant.

Introduction

The decomposition of ethane and recombination of methyl radicals form the most thoroughly studied unimolecular reaction. As such it has been frequently used as a test case for theoretical descriptions of the unimolecular decomposition process.[1,2] We present here an extension of the high pressure limit rate constant data to 2500 K, approximately doubling the temperature range previously covered. Our data show that it is possible to display the high pressure limiting rate constant at temperatures up to 2500 K as a virtually linear extrapolation of Arrhenius expressions found previously in low temperature dissociation experiments, using as activation energy the C–C bond dissociation energy of 87.76 kcal/mol.[3] In addition we report calculations of high pressure limit rate constants using two forms of RRKM theory, and investigations of various assumptions about the description of the critical configuration used in the theory. None of these rate constant calculations give a satisfactory fit to the temperature dependence of the data from 250 to 2500 K, although ACM calculations do provide a reasonable fit at least up to 1500 K.[2]

Experimental High Pressure Limit Data

We reported[4] an experimental measurement of the rate of ethane decomposition behind incident shock waves with $1330 < T < 2500$ K and $1.1 < \rho < 4.4 \times 10^{-6}$ mol/cm^3. In that report the data was extrapolated to the low pressure limit, and a discussion of the available data for the limiting behavior of this reaction at low pressures was presented. We now consider the extrapolation of our data to high pressure limiting values and compare our results with those from previous investigations. The extrapolation to $P = \infty$ was done initially using Emanuel's[5] tabulated Kassel integrals with $S = 12$, $E_0 = 87.76$ kcal/mol[3], an energy transfer efficiency of 0.07 for Ar relative to C_2H_6, and a strong-collision deactivation cross section (from viscosity data) of 0.30 nm^2. This value of S was used following Lin and Back,[6] who found that $S = 12$ gave the best RRK fit to their experimental ethane decomposition falloff curves at $910 < T < 1000$ K. Temperature-dependent S expressions such as $S = E_{vib}/RT$ did not give as good results as $S = 12$. Figure 1 shows a line describing our experimental rate data and the RRK-extrapolated high pressure limit, which is given by the expression $\log (k_\infty/s^{-1}) = 16.85 - 19700/T$. In view of the fact that S and the deactivating collision rate are expected to be temperature dependent, but in a presently still uncertain way, meaningful error limits cannot be assigned to this expression.

Also shown in Figure 1 are the k_∞ results of earlier experiments on ethane dissociation[6-14] and the results of two high temperature investigations of methyl recombination.[15,16] It would appear that all studies of the C_2H_6 dissociation rate are in satisfactory agreement with one another and show, collectively, a dependence upon temperature in accord with simple theoretical expectations. One should note, however, that the RRK extrapolation is quite large in our temperature range, exceeding three orders of magnitudes at 2500 K, even though the pressures were about half atmospheric.

For comparison with the many reported studies of CH_3 recombination near room temperature[17-28] it is expedient to convert dissociation rate constants to recombination rate constants, using standard thermochemical properties.[29,30] High pressure limit recombination rate constants from 250

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